UNPUBLISHED PRELIMINARY DATA

Semi-Annual Status Report

[redacted]

to

National Aeronautics and Space Administration

for

Research Grant NsG-247-62 to Florida State University

by
Leo Mandelkern
Principal Investigator
March 1, 1965

The major research area of this program has been concerned primarily with the fundamental acts of crosslinking polymers by high energy ionizing radiation. Of major concern has been the dependence of the crosslinking efficiency, radiochemical acts, and resultant isotropic network properties on the state of the system at the time the crosslinks were introduced. The states being studied are the completely amorphous states, states of unoriented crystallinity, including very high crystallinity, and the axially oriented crystalline state. The high level of crystallinity is obtained by very long times of crystallization at elevated temperatures. Primary attention, up to now, has been given to studies of the properties of polyethylene. Although preliminary and explanatory experiments were performed with unfractionated material in order to develop techniques, the results analyzed and reported were accomplished with fractions which encompassed a wide range in molecular weights. The utilization of molecular weight fractions helps clarify the problem, particularly in controlling and varying the amount of crystallinity and in the analyses of the partitioning between sol and gel. Some of the results obtained to date are summarized in the following published papers:

1) "Irradiation Crosslinking of Polyethylene: Relative Efficiency in Crystalline and Amorphous States", J. Polymer Sci., 2B, 511 (1964).

2) "Irradiation Crosslinking of Polyethylene: The Temperature Dependence of Crosslinking in the Crystalline and Amorphous States", J. Am. Chem. Soc., 86, 3529 (1964).

(3) "A Comparison of the Crosslinking of Highly Oriented and Non-Oriented Crystalline Polyethylene by Ionizing Radiation", J. Polymer Sci., 2, 1019 (1964).

One of the major conclusions to date has been the enhanced cross-linking efficiency, as manifested by the amount of gel formed, in the highly crystalline polymer at temperatures about 90°C. To further investigate the basic reason for this rather new observation, an elucidation of the radiochemical acts involved and their dependence on the state of the system and the temperature of irradiation has been undertaken. We are, therefore, in the process of measuring the disappearance of vinyl unsaturation and the formation of trans unsaturation by infra-red techniques as well as the amount of hydrogen evolution as it depends on the radiation dose, the temperature and the state of the system. To date the experimental techniques have been developed and some preliminary conclusions have been made. By assuming that the rate of vinyl decay follows first-order kinetics, it is found that for unfractionated polyethylene the rate constant is essentially independent of temperature for highly crystalline material. At the temperature at which the highly crystalline and completely molten polymer can be compared, the rate constant for the latter state is about 40% less. The formation of trans-vinylene has been measured in the highly crystalline sample at 25° and 133°C. A 50% increase in unsaturation per unit dose is observed at the higher temperature. A similar trend has been observed for a molecular weight fraction M_η = 200,000.

Previously published results from this laboratory indicated the possibility that chain scission processes may play an important role during the irradiation of highly crystalline polyethylene at room temperature. To further explore this possibility intrinsic viscosity measurements as a function of dose of highly crystalline polymers irradiated in the pre-gelation region have been undertaken. The results to date on two molecular weight fractions indicate that in the crystalline state there is significantly more scission after irradiation at 25°C than at 100°C, if there is any scission at all at the latter temperature. These experiments are being continued with particular emphasis on lower molecular weight samples where the crystalline morphology is more clearly defined. A theoretical analysis of this problem has been undertaken so that the relative amount of chain scission per unit dose can be more quantitatively described.

The studies into the molecular reasons for the enhanced crosslinking in highly crystalline polyethylene above 90°C is continuing. The thesis that molecular motions, possibly rotation around the chain axis is involved, is being investigated. Preliminary nuclear magnetic resonance studies are consistent with this mechanism but are not as yet definitive. This work is being continued and it is also planned, in this connection, to study the infra-red absorption spectra of highly crystalline polyethylene as a function of temperature.